

## 3 Homogeneous Nucleation

### 3.1 Importance of Homogeneous Nucleation

Condensation in the supersaturated state was first observed during the last century in the expansion of the superheated steam jet and the famous cloud chamber experiments of Wilson (1897). Nucleation is important in many of areas of science including atmospheric physics and technology. Nucleation can occur from a vapor or liquid phase. Cloud formation has implications in the atmosphere as well as in certain manufacturing processes. In material science, the properties of films and casting may depend on the grain structure caused by the nucleation mechanism. The safety of a nuclear reactor needs the understanding of nucleation problems especially when the overheating of its reactor core occurs (Williams and Loyalka, 1991). Superconductors may be used as high current transmission lines; cooled by liquid helium or liquid nitrogen. But, if overheating occurs due to some reason, its cooling can be accomplished by heat transfer by boiling due to homogeneous nucleation (Brodie et al., 1977; Sinha et al., 1987). In many cases, nucleation also occurs around foreign particles: ions, large molecules, or on solid walls (heterogeneous nucleation) (Dillmann and Meier, 1989).

Irrespective of the importance of homogeneous nucleation, nucleation theory has not been considered to be successful in all cases although it has recently become to be promising.

### 3.2 Classical Nucleation Theory

Consider nucleation or condensation, at a constant temperature  $T$ , from the vapor phase by forming a liquid droplet of radius  $r$ , containing  $n$  molecules. The droplet will grow like a chemical reaction of combining vapor molecules one by one. However, we do not follow such details and treat the process thermodynamically. The nucleation process is irreversible and does not occur in thermal equilibrium, but we consider that the state of the system involved in the process is not far from equilibrium.

Let us first assume that the nucleation takes place at constant temperature and volume, so that the thermodynamical state is expressed in terms of Helmholtz free energy. Since the system is not in equilibrium, we cannot use Eq. 2.13 except for special cases when  $F$  is maximum or minimum. Therefore, Eq. 2.15 must be written, for a one-component system, as

$$U = TS - p'V' - p''V'' + \gamma A + \mu'(p')n' + \mu''(p'')n''$$

by choosing the dividing surface to make  $n^s=0$ . Now, since  $F=U-TS$ , we have

$$F = -p_l V_l - p_v V_v + \gamma A + \mu_l n_l + \mu_v n_v$$

where the subscripts,  $l$  and  $v$ , stand for the liquid and the vapor phase, respectively. Here, the total volume,  $V=V_l+V_v$ , and the total number of molecules in the system,  $n_l+n_v$ , are assumed to be constant during the nucleation.

The system is initially in a vapor phase consisting of  $n_i$  vapor molecules in volume  $V$  without a liquid droplet ( $n_l=0$ ,  $V_l=0$ ). Hence, the initial Helmholtz free energy is given by

$$F_i = \mu_v(p_i) \cdot n_i - p_i V$$

where  $\mu_v(p_i)$  is the initial chemical potential of the vapor phase at the initial pressure  $p_i$ . (Remember that  $T$  remains constant.) In the final state,  $n$  vapor molecules out of  $n_i$  form only one liquid droplet of radius,  $r$ , ( $n=n_l$ ) under the constant total volume and  $V_l=(4\pi/3)r^3$ . If the pressure of the liquid phase is denoted by  $p_l$  and the final vapor pressure by  $p_f$ , the final Helmholtz free energy is given by

$$F_f = \mu_v(p_f) \cdot (n_i - n) + \mu_l(p_l)n - p_f(V - V_l) - p_l V_l + 4\pi r^2 \gamma$$

where the surface tension,  $\gamma$ , is assumed not to depend on  $r$ , ignoring Eq. 2.21. Now, we can find the change of the free energy in nucleation,  $(\Delta F)_{T,V}=F_f-F_i$ . Noting that  $\mu_v(p_f)-\mu_v(p_i)=k_B T \ln(p_f/p_i) \approx -k_B T(1-p_f/p_i)$ , since  $p_f/p_i \approx 1$ , or, equivalently, that  $p_i \approx p_f$ , we obtain

$$(\Delta F)_{T,V} = (\mu_l - \mu_v)n - (p_l - p_f)V_l + 4\pi r^2 \gamma \quad (3.1)$$

Since experiments on nucleation are usually made under constant pressure, we convert Eq. 3.1 to the Gibbs free energy. While in the Helmholtz free energy no work is done on surroundings because of the constant total volume, the Gibbs energy must include this work to keep the pressure of the system constant. This conversion is made by adding (equivalently eliminating) the small second term,  $(p_l - p_f)V_l$  (Rao et al., 1978). This term is the reversible work (Reichl, 1980, p. 39). Thus, the Gibbs free energy of formation of a liquid droplet of size  $n$  from  $n$  vapor molecules is given by, denoting by  $p$  the constant pressure of the system,

$$\Delta G_n(p, T) = (\mu_l - \mu_v)n + 4\pi r^2 \gamma \quad (3.2)$$

We may rewrite the second term in terms of  $n$ , as follows:

$$4\pi r^2 \gamma = \alpha n^{2/3}, \quad \text{with } \alpha = 4\pi(3v_l/4\pi)^{2/3} \gamma \quad (3.3)$$

where  $v_l$  is the volume per molecule in the liquid phase at the temperature  $T$  and pressure  $p_l$ . The assumption that the Gibbs free energy of formation is given by Eq. 3.2 is called the capillarity approximation since it contains the surface tension as a part.

If the vapor is unsaturated, the vapor pressure is lower than the equilibrium value at  $T$  and thermodynamics requires that  $\mu_v < \mu_l$ , so that  $\Delta G_n$  of Eq. 3.1 is an increasing function of  $n$  for any  $n$ . This implies that the nucleation or condensation is not spontaneous.

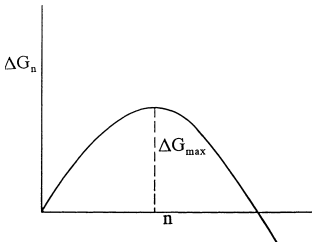
If the vapor is supersaturated,

$$\mu_v > \mu_l \quad (3.4)$$

Equations 3.2 and 3.3 then show that, if  $n$  is small,  $\Delta G_n$  can be positive and increases with  $n$ , but as  $n$  increases further, the first term becomes to dominate and  $\Delta G_n$  decreases with increasing  $n$ . Thus, as seen in Fig. 3.1, there is a maximum in  $\Delta G_n$ , denoted by  $\Delta G_{\max}$ , which occurs at a value of  $n$ , denoted by  $n_c$ . This is called the critical size of  $n$ , and the liquid drop can spontaneously grow to a macroscopic size only when the size of the droplet is larger than this value of  $n$ . Therefore,  $\Delta G_{\max}$  is a barrier height of the activation energy for nucleation of a liquid drop. A real nucleation therefore requires an initial formation of a cluster or an embryo due to some other mechanism, called thermal fluctuations (or, if the temperature is very low, quantum fluctuations). The problem of calculating the rate of nucleation is essentially to estimate the rate at which fluctuations occur so that a nucleus of adequate size is produced.

We may write

$$\mu_l - \mu_v = -k_B T \ln(p/p_0) = -k_B T \ln S \quad (3.5)$$



**Fig. 3.1** Variation of the free energy of formation of a reversible nucleus in a supersaturated vapor phase.

where  $p_o$  is the saturation vapor pressure in equilibrium with the liquid phase over a plane interface at  $T$  and  $S$  is called the degree of supersaturation ( $S > 0$ ). Now, the number density of  $n$ -clusters (clusters of size  $n$ , or  $n$ -mers) in thermal equilibrium is given by

$$c_n = c_1 \exp(-\Delta G_n/k_B T) = c_1 \exp\{-(n \ln S + \alpha n^{2/3}/k_B T)\} \quad (3.6)$$

where  $c_1$  is the number density of monomers (single unclustered molecules), assuming that monomers are predominant in number compared with clusters of any size.

However, the supersaturated system is not in thermal equilibrium and nucleation is an irreversible process. As referred before, the nucleation occurs by combining the vapor molecule,  $A_1$ , one by one and we consider the kinetics of the reaction chain,  $A_j + A_1 \rightleftharpoons A_{j+1}$  ( $j=1, 2, 3, \dots$ ). The number density,  $f(n, t)$ , of nuclei of size  $n$  at time  $t$  must be determined by the rate equation:

$$\begin{aligned} \frac{\partial f(n, t)}{\partial t} = & \beta A_{n-1} f(n-1, t) + \alpha_{n+1} A_{n+1} f(n+1, t) \\ & - \beta A_n f(n, t) - \alpha_n A_n f(n, t) \end{aligned} \quad (3.7)$$

where  $A_n$  is the area of an  $n$ -mer,  $\alpha_n$  is the evaporation rate per unit area,  $\beta$  is the collision frequency with vapor molecules (monomers) per unit area. We assume that the sticking coefficient of the colliding molecules is unity and  $\alpha_n$  and  $\beta$  are constant with time. If we write

$$J(n, t) = \beta A_n f(n, t) - \alpha_{n+1} A_{n+1} f(n+1, t) \quad (3.8)$$

we have

$$\frac{\partial f(n, t)}{\partial t} = J(n-1, t) - J(n, t) = -\frac{\partial J(n, t)}{\partial n}, \quad (3.9)$$

where the Taylor series expansion is used to obtain the last expression by assuming that  $n$  is continuous. Thus, the rate equation is an equation of continuity with a flux (cluster current density) defined by Eq. 3.8, in the population space,  $n$ . We note from Eq. 3.9 that  $J(n, t)$  is independent of  $n$  and  $t$  at a stationary state. However, the stationary state is artificial and is assumed to occur provided each growing nucleus, once formed, is removed from the system. Therefore  $f(n, t)=0$  for  $n \gg n_c$ , and its mass is replenished by an equal mass of vapor molecules.

In Eq. 3.8, the collision frequency per unit area is given by the well-known quantity,  $n_v \langle v \rangle_{av}/4$ , so that

$$\beta A_n = 4\pi r^2 p / (2\pi m k_B T)^{1/2} \quad (3.10)$$

where  $p$  is the supersaturated vapor pressure and  $m$  is the mass of the vapor molecule. At the barrier peak of  $\Delta G_n$ , the vapor and the liquid drop are in equilibrium, so that the detailed balance holds.

$$\beta A_n c_n = \alpha_{n+1} A_{n+1} c_{n+1} \quad (3.11)$$

Thus, at  $\Delta G_{\max}$  ( $n=n_c$ ), noting that  $J$  in Eq. 3.8 is constant,

$$J = \beta A_n c_n \left( \frac{f(n)}{c_n} - \frac{f(n+1)}{c_{n+1}} \right) = -\beta A_n c_n \frac{\partial f(n)}{\partial n} \frac{1}{c_n} \quad (3.12)$$

Here we have omitted  $t$  in  $f(n,t)$ . Remember that  $c_n$  is the equilibrium number density of an  $n$ -mer. This equation leads to

$$J^{-1} d(f(n)/c_n) = -(1/\beta A_n c_n) dn \quad (3.13)$$

Here  $J$  and  $f(n)$  are unknown, but  $J$  is a constant. Now, we expand  $\Delta G_n$  into the Taylor series at  $n_c$ , noting that  $\Delta G_n$  is maximum at  $n=n_c$ ,

$$\Delta G_n = \Delta G_{\max} + \frac{1}{2} (\partial^2 \Delta G_{\max} / \partial n_c^2) \cdot (n - n_c)^2 + \dots \quad (3.14)$$

Substituting this expansion into  $c_n$  on the right-hand side of Eq. 3.13, we integrate it around  $n_c$  by truncating higher terms. This integration involves a Gaussian function so that the value will not be much affected by extending the integration limits to those from  $n=1$  to some large number  $N$  ( $> n_c$ ). By assuming that  $f(1)/c_1=1$  and  $f(N)/c_N=0$  for  $N \gg n_c$  because of the assumption of the stationary state (see also McDonald, 1963), we have

$$J = \beta A_{n_c} c_1 \sqrt{-\frac{1}{2\pi k_B T} \frac{\partial^2 \Delta G_{\max}}{\partial n_c^2}} e^{-\frac{\Delta G_{\max}}{k_B T}} \quad (3.15)$$

Now, by using Eqs. 3.2, 3.3, and 3.10 this can be written as

$$J_{\text{classical}} = \frac{1}{3} \sqrt{\frac{\alpha}{\pi}} \frac{p_0^2 \alpha / \gamma}{\sqrt{2\pi m} (k_B T)^2} S^2 e^{-\frac{4}{27} \left( \frac{\alpha}{k_B T} \right)^3 \frac{1}{\ln^2 S}} \quad (3.16)$$

Hence, the rate of droplet formation is expressed only in terms of measurable bulk quantities as a function of temperature and the degree of supersaturation.

In order to get some idea of the rate of nucleation, we estimate Eq. 3.16 for water at  $0^\circ\text{C}$ . Taking  $v_\ell = 18 \text{ cm}^3/\text{mol}$ ,  $p_o = 4.6 \text{ mm Hg}$ , and  $\gamma = 72 \text{ ergs/cm}^2$ , we have

**Table 3.1** Variation of the exponential function of Eq. 3.17 for various  $S$ 

| $S$              | 2.0        | 2.5        | 3.0        | 3.5       | 4.0        | 4.2        | 4.5        |
|------------------|------------|------------|------------|-----------|------------|------------|------------|
| $J_{\text{cl.}}$ | $10^{-75}$ | $10^{-32}$ | $10^{-15}$ | $10^{-5}$ | $10^{0.3}$ | $10^2$     | $10^{4.2}$ |
| $dJ/dS$          | $10^{-72}$ | $10^{-29}$ | $10^{-13}$ | $10^{-4}$ | $10^{1.0}$ | $10^{3.3}$ | $10^{5.3}$ |

$$\dot{J}_{\text{cl., water at } 0^\circ\text{C}} \simeq 10^{24+0.87 \ln S - \frac{47.8}{\ln^2 S}} / \text{cm}^3 / \text{sec} \quad (3.17)$$

Table 3.1 illustrates how the rate of nucleation changes with the degree of supersaturation. The quantity,  $dJ/dS$ , stands for the rate of  $J$  per unit change of  $S$ . It shows that  $J$  suddenly increases very rapidly at around  $S=4.2$ .

Supersaturation can be achieved by lowering the temperature of the vapor. When the temperature is gradually reduced, the rate of nucleation first slowly increases, but eventually the rate increases rapidly, when nuclei of critical radius start to be formed by thermal fluctuations. This temperature is called the homogeneous nucleation temperature.

Some experimental results, like those of Sander and Damköhler (1943) on water vapor, Sharaf and Dobbins (1982) for water vapor in the presence of argon, etc. are in a reasonable agreement with Eq. 3.16.

It is interesting to note that the classical theory is applicable even for liquid helium, helium 3, in which bubbles are formed when locally heated (Lezak et al. 1988).

However, with the increasing refinement of experimental techniques, the classical homogeneous nucleation theory was found to be significantly incorrect, differing from experiments by a factor of several orders of magnitude and many new theories were proposed (for instance, Zettlemoyer, 1977; Oxtoby, 1992). In particular, the temperature dependence of the predictions can be widely inaccurate. As an example, Huang et al. (1989) found that their experimental results with n-nonane were closest to the prediction of the classical theory, but they differ by a factor of  $2 \times 10^{-5}$  at  $T=233\text{K}$  to  $4 \times 10^3$  at  $315\text{K}$ .

### 3.3 New Approaches to Nucleation Theory

First we note that  $\Delta G_n$ , Eq. 3.2, is not quite correct. When  $n=1$ , Eq. 3.6 suggests that  $\Delta G_{n=1} \neq 0$ . Therefore, we must make a correction by adding some constant with respect to  $n$ . Even though it is not important for large  $n$ 's, such self-consistency is important. We have, as a simplest choice (Girshick and Chiu, 1990),

$$\Delta G_n = (\mu_\ell - \mu_v)(n-1) + \alpha(n^{2/3} - 1) + C, \quad (3.18)$$

where  $C$  is some constant, which was obtained by statistical mechanics. There are other inconsistencies in the capillarity approximation, related to the law of mass

action (Zettlemoyer, 1977, p. 11). Ford, Barrett, and Lazaridis (1993) used an approach of statistical mechanics for  $\Delta G_n$  and obtained the rate of nucleation. The results showed an improvement in some cases, but not in some other cases.

As noted before, the prediction of Eq. 3.16 with Eq. 3.2 shows in various cases a discrepancy of several orders of magnitude from experimental results. This indicates that important contributions to the cluster free energy has been omitted in Eq. 3.2. Lothe and Pound (1962) for example considered the clusters as a spherical “super molecule” and calculated contributions to  $\Delta G_n$  from its translational and rotational degrees of freedom in terms of statistical mechanics. However, the theoretical results on homogeneous nucleation rates from water vapor are larger than those of certain cloud-chamber observations by a factor of  $10^{17}$ . Reiss et al. (1968) considered oscillations of the center of mass of a spherical droplet with fixed boundaries. This model predicts greater than the classical model by a factor of  $10^3$  to  $10^6$ , disagreeing again with experiments.

Now, if a droplet has some degree of freedom of motion we can construct the corresponding partition function,  $q$ . Then, the free energy can be calculated by adding  $-k_B T \ln q$ . Thus, including this contribution into the drop model of the capillarity approximation, Dillman and Meier (1991) suggested that

$$\Delta G_n / k_B T = -n \ln S + \kappa_n \alpha n^{2/3} / k_B T + \tau \ln n - \ln q \quad (3.19)$$

The size-dependent function,  $\kappa_n$ , describes the deviation of the surface energy of the cluster from that of a macroscopic droplet and

$$\kappa_{n \rightarrow \infty} = 1 \quad (3.20)$$

The third and fourth terms of Eq. 3.19 correspond to the translational, rotational, and vibrational degrees of freedom as well as the configurational effect (see Zettlemoyer, 1977, p. 131). Dillmann and Meier (1991) derived a formula for  $\kappa_n$ ,  $\tau$ , and  $q$ , which can be determined in terms of well-known handbook properties. From Eqs. 3.6 and 3.19, the number density and the pressure of the vapor phase are given by

$$\rho = \sum_{n=1}^{\infty} n c_1 e^{-\frac{\Delta G_n}{k_B T}} = q c_1 \sum_{n=1}^{\infty} \exp \left[ \frac{-\kappa_n \alpha n^{2/3} + n \ln S}{k_B T} - (\tau - 1) \ln n \right] \quad (3.21)$$

and

$$p = q c_1 k_B T \sum_{n=1}^{\infty} \exp \left[ \frac{-\kappa_n \alpha n^{2/3} + n \ln S}{k_B T} - \tau \ln n \right] \quad (3.22)$$

respectively. These equations can be assumed to hold even at the critical point (Vincenti-Missoni et al., 1969; Stauffer et al., 1971), where the surface tension vanishes. Thus,  $p_c / \rho_c k_B T_c$  is a function of  $\tau$  only. Dillmann and Meier (1991)

obtained  $\tau \approx 2.2$  for ordinary substances. Then, from Eq. 3.21 the value of  $qc_1/\rho_c$  can be found to be  $\sim 1.5$ . They assumed that  $\tau$  and  $qc_1/\rho_c$  do not depend on the temperature. In order to determine  $\kappa_n$ , they write

$$\rho = qc_1 \sum_{n=1}^{\infty} \left( \frac{p}{p_o} \right)^n \exp \left[ -\kappa_n \frac{\alpha}{k_B T} n^{2/3} - (\tau - 1) \ln n \right] \equiv \sum_{n=1}^{\infty} A_n(T) p^n \quad (3.23)$$

where

$$A_n(T) = \frac{qc_1}{p_o^n} \exp \left[ -\kappa_n \frac{\alpha}{k_B T} n^{2/3} - (\tau - 1) \ln n \right] \quad (3.24)$$

Now, Eq. 3.23 may be compared with the equation of state,

$$p/\rho = k_B T + B(T)p + C(T)p^2 + \dots, \quad (3.25)$$

to find  $\kappa_n$ . However, there is a simplifying relation (Dillman and Meier, 1989):

$$\kappa_n = 1 + \alpha_1 n^{-1/3} + \alpha_2 n^{-2/3} \quad (3.26)$$

so that  $\kappa_n$  is known for all  $n$  if  $\alpha_1$  and  $\alpha_2$  are known. From Eqs. 3.21 and 3.25, we find

$$\kappa_1 = -(k_B T / \alpha) \cdot \ln(p_o / qc_1 k_B T) \quad (3.27)$$

$$\kappa_2 = -(k_B T / \alpha 2^{2/3}) \cdot \ln[-(p_o / qc_1 k_B T)^2 2^{\tau-1} qc_1 B(T)] \quad (3.28)$$

and by using Eq. 3.26  $\alpha_1$  and  $\alpha_2$  can be obtained. More specifically for the computation, we need  $\gamma(T)$  of  $\alpha$  and  $B(T)$ . For example, for water,

$$\gamma(T) = 93.6635 + 0.009133T - 0.000275T^2 \text{ dyn/cm} \quad (3.29)$$

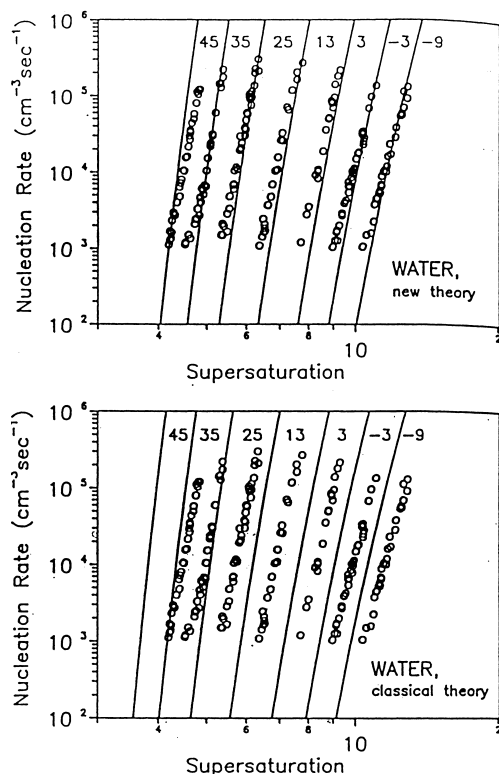
$$B(T) = 17.1 - 102.9/T_r^2 - 33.6 \cdot 10^{-3} T_r \exp(5.255/T_r) \text{ cm}^3/\text{mol} \quad (3.30)$$

where  $T_r = T/T_c$ , the reduced temperature. Therefore,  $\kappa_n$  can be found for water as shown in Table 3.2. The quantity,  $\kappa_n$ , is greater than unity for polar molecules ( $\kappa_1$  can be as large as 1.6) and depends on temperature very strongly in some cases.

**Table 3.2** Values of  $\kappa_n$  for water at 0°C.

| $n$        | 1    | 2    | 5    | 10   | 100 | 1000 |
|------------|------|------|------|------|-----|------|
| $\kappa_n$ | 0.91 | 1.15 | 1.21 | 1.25 | 1.2 | 1.12 |





**Fig. 3.2**  $J$  versus  $S$  for water (Dillmann and Meier, 1991, with permission from AIP).

Applying Eq. 3.19 to Eq. 3.16, Dillmann and Meier (1991) obtained the rates of nucleation for various substances in a wide range of temperatures. Their theory gives a better prediction of observed rates than the classical one. Figure 3.2 gives an example of this for water.

### 3.4 Atomistic Model of Nucleation Theory

If the critical droplet size,  $n_c$ , in nucleation is small and the temperature is low so that molecules of the droplets are not so thermally excited, the atomistic model may be able to handle the Gibbs free energy of formation,  $\Delta G_n$ , without knowing macroscopic parameters, such as surface tension. Examples are nonpolar molecules, such as argon (Hoare et al., 1980) and nitrogen (Pal and Hoare, 1987; Wegener, 1987). There are no nucleation experiments on helium condensation from the gas phase.

In both argon and nitrogen, the classical capillarity approximation with macroscopic values of surface tension could qualitatively predict the experimental

results of nucleation rates, but quantitatively failed. In the case of argon, the nucleation theory involves around 20-mers and there is hardly a distinction between surface and bulk free energies.

The atomistic model begins with the assumption of intermolecular potential, like of the Lennard-Jones type.

$$V(\mathbf{r}_i, \mathbf{r}_j) = \frac{a}{|\mathbf{r}_i - \mathbf{r}_j|^{12}} - \frac{b}{|\mathbf{r}_i - \mathbf{r}_j|^6} \quad (3.31)$$

where  $a$  and  $b$  are constants and  $\mathbf{r}_i$  and  $\mathbf{r}_j$  are positions of any pair of molecules in the  $n$ -mer cluster. Nitrogen molecules are assumed to be spherical. The total potential energy is then given by

$$V(n) = \sum_{i=1}^n \sum_{j>i} V(\mathbf{r}_i, \mathbf{r}_j) \quad (3.32)$$

The molecular configuration (hexagonal or cubic closed-packed or the like) of the possibly spherical cluster is determined so that  $V(n)$  is minimum. Then, the degrees of freedom of motion are introduced to the  $n$  molecules around their equilibrium positions, including the translational and rotational motion as a whole. Assuming these motions are separable, the intermolecular vibrations are treated by the harmonic oscillator approximation. For nitrogen, each molecule has two atoms which can exhibit vibration and rotation inside each molecule and contribute to the Gibbs energy. The total contributions can be found from the partition function,  $Q(n)$ , standing for all of these degrees of freedom and including the factor  $\exp(-V(n)/k_B T)$ . The Gibbs free energy is approximated by

$$\Delta G_n(p, T) = -k_B T [\ln Q(n) - n \ln Q(1) + (n-1) \ln S] \quad (3.33)$$

Using this Gibbs free energy in Eq. 3.15, it gave agreeable results with experiments on argon and nitrogen.

## Exercises

- 3.1 From Eqs. 3.1 and 3.2 find the critical value of  $n$ . What is the probability that an embryo will appear with the critical value of  $n$  by thermal fluctuation?
- 3.2 Consider the formation of a liquid droplet in the supersaturated vapor phase. Show that the critical radius,  $r^*$ , of an embryo for nucleation is given by

$$r^* = 2\gamma v_\ell / (k_B T \ln S)$$

where  $S$  is the degree of supersaturation and  $v_l$  is the volume per molecule in the liquid phase. The above relation is called as the Kelvin equation (see Exercise 2.4).

- 3.3 Derive Eq. 3.5.
- 3.4 Establish Eq. 3.15.
- 3.5 Find Eq. 3.16 from Eq. 3.15.
- 3.6 Calculate of the critical radius of nuclei in homogeneous nucleation for water  $t=0^\circ\text{C}$  ( $S = 4.2$ ). How many water molecules do you expect in this critical nucleus?
- 3.7 Discuss the bubble formation in the bulk water phase.
- 3.8 Consider an electron in liquid helium. The electron cannot attach to helium atoms. Assume that the helium atoms behave like hard balls to the electron. How can the electron be trapped in liquid helium? Consider the external pressure is one atmosphere.
- 3.9 Find the partition function for the translational motion of an embryo in nucleation in a three-dimensional vapor.

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